Photodegradation of Metolachlor in Natural and Constructed Wetlands

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ABSTRACT

Agricultural wetlands receive a variety of nutrients and synthetic organic contaminants (SOCs), such as pesticides, from agricultural activities. Constructed wetlands have been proposed as a cost-effective and sustainable treatment method for the retention and degradation of SOCs in agricultural ecosystems. Since wetlands have a high ability to retain and process material, it is reasonable to assume that constructed wetlands can act as a buffer between agricultural areas and receiving waters, thereby mitigating the impact of pesticides in runoff. One important pathway in wetlands, photolysis, is capable of degrading these substances through sunlight driven reactions. Naturally occurring substances, such as iron, dissolved organic matter (DOM), and nitrate, may accelerate the photolytic degradation of SOCs through a photosensitized process called indirect photolysis. The purposes of this study were: (1) to determine the nature and abundance of photosensitizers (DOM, nitrate, and iron) present in one natural wetland and three constructed wetlands, (2) to investigate the sunlight induced degradation of metolachlor in the four wetland waters, and (3) to promote the photodegradation of metolachlor in constructed agricultural wetlands through the addition of iron to wetland waters. Water samples were collected from one natural and three constructed wetlands (Old Woman Creek, Olentangy River Wetland Research Park, Waterman Farm Wetland, and Defiance County Wetland) and were analyzed for pH, UV-Vis absorbance, total organic carbon, nitrate, and total iron concentration. Photodegradation of the herbicide metolachlor was carried out in the wetland waters to examine the effects of natural photosensitizers on the photofate of metolachlor. Metolachlor degradation was enhanced 58 to 141 times at pH 4 and 2 to 11 times at pH 8 in wetland waters compared to direct photolysis in deionized

water, with Old Woman Creek water acting most effectively. The addition of 2 to 10 µM of iron promoted metolachlor degradation in Old Woman Creek water by 37-100% at pH 4, while no significant enhancements were observed for other wetland waters. Current studies are optimizing the photodegradation through altering the concentrations of different photosensitizers.

INTRODUCTION

Overview

The estimated usage of the herbicide metolachlor in the United States is 60-65 million pounds active ingredient per year (Rivard, 2003). Metolachlor is used to control specific broadleaf weed species and annual grassy weeds, and is primarily applied to corn, soybean, peanuts, sorghum, potatoes, cotton, safflower, and woody ornamentals, (PMEP, 2008). According to the California Department of Pesticide Regulation, metolachlor is or has been sold under various trade names, such as Bicep, Codal, Cotoran multi, Dual, Dual 8E, Metelilachlor, Milocep, Ontrack 8E, Pennant, Pennant 5G, Primagram, and Primextra (Rivard, 2003).

Agricultural nonpoint source (NPS) pollution is a serious threat to water quality and is diffuse and difficult to treat. Nutrients and agrochemicals, such as pesticides and herbicides, are the main detrimental agricultural NPS constituents. Decades of agricultural fertilizer application have resulted in a global problem due to excessive nitrate levels in surface waters. Subsequent discharge has increased surface water nitrate levels in the Upper Mississippi River Basin, causing widespread seasonal hypoxia in the Gulf of Mexico (Turner and Rabalais, 1994). Agrochemicals post potential health risks to humans and wildlife, and recent findings have shown the presence of pesticides in drinking water supplies.

Metolachlor has been shown to infiltrate ground and surface waters at concentrations ranging from 0.01 to 0.40 μg/L (Dimou et al., 2005). A 1988 study of surface and ground water in the United States found metolachlor in 2091 of 4161 surface

water samples, and in 13 of 596 groundwater samples. The 85th percentile of all non-zero samples was 12 µg/L for groundwater (WHO, 1996).

Constructed wetlands have been proposed as a cost-effective and sustainable treatment method for NPS pollutants such as nutrients and chemicals resulting from agricultural activity. There has been recent interest in the application of constructed wetlands for treating synthetic organic contaminants (SOCs), such as pesticides, but very little is known of the processes that lead to the retention or degradation of these chemicals in wetlands. Since wetlands have a high ability to retain and process material, it is reasonable to assume that constructed wetlands can act as a buffer between agricultural areas and receiving waters, thereby mitigating the impact of pesticides in runoff.

This study examined how one important pathway, photolysis, can be effectively applied to degrade metolachlor in constructed agricultural wetlands. Direct photodegradation of a contaminant occurs by a contaminant's absorption of sunlight leading to its degradation. Indirect photolysis occurs when dissolved organic matter (DOM), iron, and nitrate in the wetland absorb sunlight and create free radicals that react with a contaminant to promote degradation, a process called photosensitization. Indirect photolysis is important for compounds that cannot absorb sunlight, but both direct and indirect photolysis often occur simultaneously. The physical characteristics of agricultural wetlands, such as shallow depth and large surface area, provide ample sunlight exposure and penetration for photochemical reactions to occur.

Various studies have shown that indirect photodegradation of chloroacetamide compounds such as metolachlor can occur in natural waters (Dimou et al., 2005; Cawley,

2005; Kochany and Maguire, 1994). The study by Kochany and Maguire (1994) showed that sunlight photodegradation of metolachlor was a relatively slow process with half lives of 22 and 205 days in summer and winter, respectively. In addition, Miller and Chin (2002, 2005) found that wetland waters promoted the photodegradation of the pesticide carbaryl and the herbicide alachlor through indirect photolysis. Furthermore, iron plays an important role in sunlight induced photochemistry (Gao and Zepp, 1998; Rose and Waite, 2003; Southworth and Voelker, 2003; White, et al., 1998). However, few studies have been carried out to examine the addition of iron to wetland waters to promote sunlight induced photodegradation of SOCs. I hypothesized that the presence of photosensitizers from wetland waters accelerates metolachlor photodegradation, and seeding the waters with iron, an environmentally "benign" substance, will further enhance metolachlor degradation by indirect photolysis.

Proposal Objectives

The purposes of this study were: (1) to determine the nature and abundance of photosensitizers (DOM, nitrate, and iron) present in one natural wetland and three constructed wetlands, (2) to investigate the sunlight induced degradation of metolachlor in the four wetland waters, and (3) to promote the photodegradation of metolachlor in constructed agricultural wetlands through the addition of iron to wetland waters.

MATERIALS AND METHODS

Sample Waters Collection and Preparation

Wetland waters were collected from four locations in Ohio that capture drainage from surrounding agricultural areas. These sites include two constructed agricultural wetlands, one on Waterman Farm (WTF) on the OSU campus and the other in Defiance County (DEF), Ohio, an engineered wetland at the Olentangy River Wetland Research Park (ORW) in Columbus, Ohio, and a natural coastal Lake Erie wetland, Old Woman Creek National Estuarine Research Reserve (OWC). Sample waters from OWC were collected in April 2007 at the outlet of the wetland. Sample waters were collected from WTF, DFE, and ORW in June 2007. At WTF, water samples were collected from the small constructed wetland 10 feet from the nursery. At ORW, water samples were drawn from the Eastern constructed wetland. Three five-gallon carboys were collected from each wetland. Samples were grabbed from the surface of the wetlands using a one-liter Nalgene bottle. After collection, raw waters were acidified to pH 2.0, filtered with 0.7 μm glass fiber filter (Whatman GFF), and stored at 4°C until use.

Analytical Methods for Sample Waters Characterization

Raw water samples were analyzed for pH, DOM using a total organic carbon analyzer (TOC 5000A, Shimadzu), nitrate concentration by ion chromatography (IC; DX500, Dionex), UV-Vis absorbance by a UV-Vis spectrophotometer (Cary, Varian), and total iron concentration by inductively coupled plasma atomic emission spectrometry (ICP-ES; Vista Ax, Varian). For measuring DOM, A standard curve ($R^2 = 0.9999$) was made from reagent grade potassium hydrogen phthalate solution with concentrations of 1,

2, 5, and 10 mg/L total carbon. Samples were acidified to pH 2 with 1 M HCl, purged for 3 min with high purity air to remove inorganic carbon, and analyzed by the TOC analyzer with 3 injections. For total dissolved iron measurement, the stock standard solution used for analysis was from Inorganic Ventures, Inc. and had a starting iron concentration of 9989 μg/mL. Seven standard solutions from 0.5 to 35 μM For ICP-AES were diluted using 5% nitric acid from a stock solution. Three replicates were obtained for each standard and sample. The background for all samples and standards was a 5% nitric acid solution (Fisher Scientific, Trace Metal Grade). Nitrate was analyzed using IC consisting of a LC20 Chromatography Enclosure, ED40 Electrochemical Detector, GP50 Gradient Pump and AS40 Auto Sampler. The standards for IC were made using sodium nitrate (Fisher Certified A.C.S. Crystal) with concentrations from 1 to 200 μM. During the analysis, helium gas (Helium Compressed, 5.0 Grade) at 80 psi was used at the gas cylinder regulator, 30 psi was applied to the mobile phase of NaOH, and 570 psi on the column (AS11-4mm, DX). Mobile phase and samples were combined with a 0.5 mmol solution of NaOH from 0-18 minutes during analysis. After 18 minutes, the solution changed to 5 mmol NaOH for the duration of 18 to 22 minutes. Finally, from 22 minutes to 28.5 minutes the mobile phase consisted of a 20 mM NaOH solution. The nitrate retention time was at approximately 10 minutes. My research mentor, Ziqi He, was responsible for the nitrate and iron measurements.

Experimental Methods

The photolysis experiments utilized an arc lamp source and a photochemical reactor. The arc lamp source was a research lamp housing with built-in ignitor and a 500 W Hg (Xe) arc lamp (Oriel). The lamp was set at maximum output, and the measured

power was 3 W by a UV silicon probe (Oriel 70282) equipped with a radiant power meter (Oriel 70260). An optical filter (Oriel 51225) was used to cut off UV light below 299 nm. The light output was irradiated onto a 500 mL water-jacketed cylindrical reactor equipped where the irradiating surface is comprised of quartz. Reactor ports functioned as sampling ports, and pH was monitored using a sure-flow Ross semi-micro pH electrode (Thermo-Orion). Solution pH was manually maintained using 0.1 M NaOH (Reagent ACS, Pellets 97+%, Fisher Scientific) and 0.1 M HCl (Trace Metal Grade, Fisher Scientific). Reactions were carried out under natural (pH 8) and acidic (pH 4) conditions. A water-cooling system ISOTEMP 1006S (Fisher Scientific) kept the reactor temperature constant at 25ºC. Considering both analytical capabilities of the HPLC and concentrations relevant in wetland systems, all experiments were doped with an initial metolachlor concentration of 10 μM. Concentrations of iron (Fe^{3+}) varied from 2 to 10 μM to determine the best concentration for metolachlor photodegradation under natural conditions. These concentrations were chosen based on detection limits of ICP-AES and the solubility of iron. Experimental nitrate concentrations depended upon sample water characteristics. Approximately 1 mL of sample was withdrawn at selected times and placed in amber glass HPLC vials for analysis. Direct photolysis of compounds in deionized water and dark control experiments (without light irradiation) were performed under similar conditions. Selected experiments were run in duplicate or triplicate to ensure reproducibility.

Analytical Methods for Kinetic Experiments

Reverse phase high pressure liquid chromatography (HPLC; Hewlett Packard 1100) was used for metolachlor detection using a UV detector. An Allure C_{18} column (5

mm, 150 x 3.2 mm, Restek) was used and the analyte detected at 220 nm. The mobile phase was 25% water and 75% methanol (0.5 ml min^{-1}) with a retention time of 7 minutes.

RESULTS AND DISCUSSION

Sample Water Characterization

Table 1 shows the initial pH, DOC concentration, nitrate concentration, specific ultraviolet absorbance (SUVA) at 280 nm for pH 4 and pH 8, and the total iron concentration for the filtered sample waters. The UV-Vis absorbance spectra for the filtered sample waters at pH 4 and pH 8 are shown in Figures 1 and 2, respectively.

Table 1: Properties of Wetland Waters

	OWC	ORW	WTF	DEF
Initial pH	7.8	7.8	7.4	7.8
DOC (mg L^{-1})	4.06	7.81	7.08	10.2
Nitrate (uM)	115	123	114	22
$SUVA_{280,\ pH\ 4}$ (L m^{-1} mg^{-1})	1.67	2.20	2.31	1.45
$SUVA_{280,\ pH\ 8}$ (L m^{-1} mg^{-1})	2.09	2.41	3.05	1.70
Fe_{Total} (uM)	12.1	1.54	23	3.49

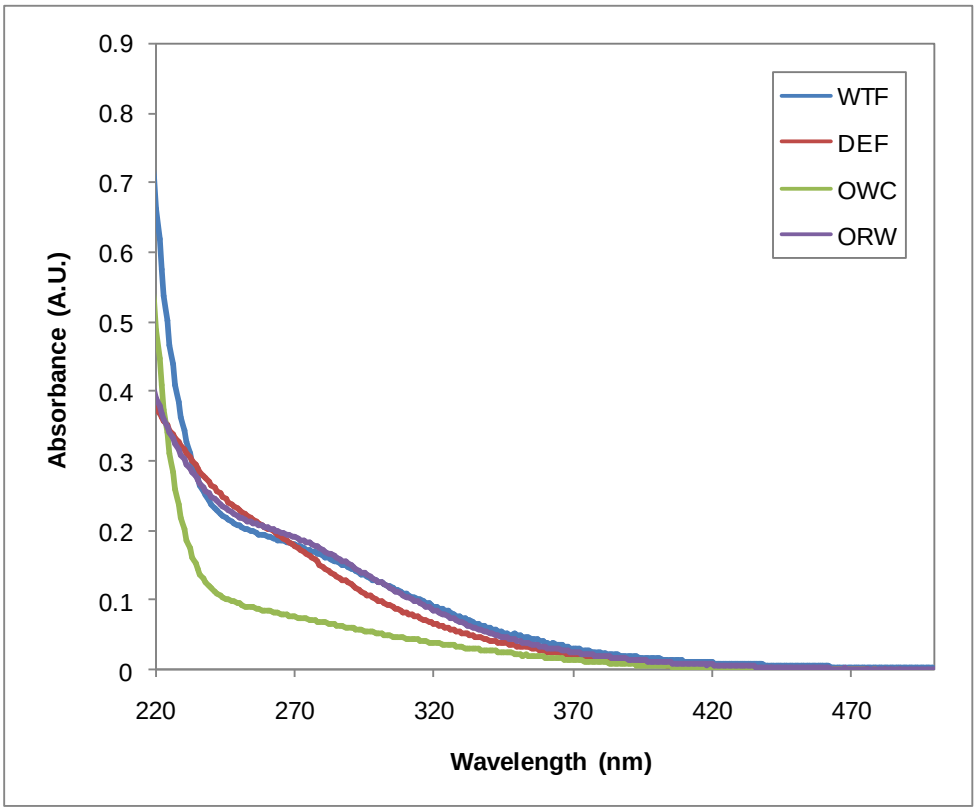

Figure 1: UV-Vis Absorbance Spectra at pH 4

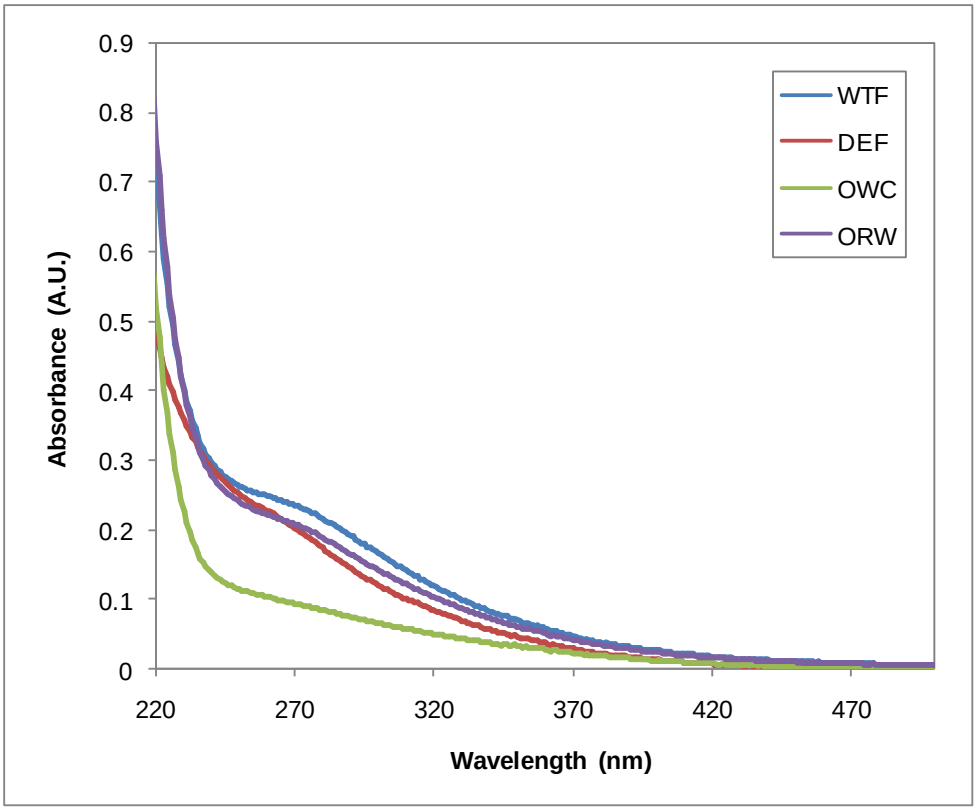

Figure 2: UV-Vis Absorbance Spectra at pH 8

The natural wetland, OWC, had the lowest DOC concentration, while DEF had the highest DOC concentration of the constructed wetlands. Nitrate concentrations were comparable for all wetlands except DEF, where the concentration was 5 to 6 times lower. As shown in Figures 1 and 2, OWC water had a much lower light absorbance above 299 nm compared to the three constructed wetland waters at both pH 4 and pH 8. $SUVA_{280}$ levels were lowest in DEF. Iron concentrations were highest in WTF and lowest in ORW.

The DOC concentration at OWC is comparable to previous studies (Miller and Chin, 2002; Miller and Chin, 2005). Additionally, published data on nitrate levels at OWC in early summer are comparable (Miller and Chin, 2002). Iron concentrations found in a previous study by Miller and Chin (2005) show lower concentrations at OWC (0.2 µM total iron). The nitrate concentration at ORW is comparable to a "low-nitrate

concentration year" seen at the wetland (Mitsch, et al., 2005). Other data are unavailable for ORW. No information on WTF is available for direct comparison. For DEF, a previous study by Miller and Chin (2005) shows comparable DOC concentrations, while our measured nitrate and iron concentrations are slightly higher. Generally, wetlands have TOC concentrations up to 40 mg/L and DOC can be up to 25 mg/L (Kaldec and Knight, 1996). Metals, such as iron, may be present in wetlands ranging from 0-90 µM (Kaldec and Knight, 1996).

Photodegradation of Metolachlor in Wetland Waters

As shown in Figure 3, metolachlor undergoes slow direct photolytic degradation. Since the speciation of metolachlor doesn't change from pH 4 to pH 8, direct photolysis of metolachlor was carried out at natural conditions (pH 8). There is no change in degradation rate between pH 4 and pH 8 (data not shown).

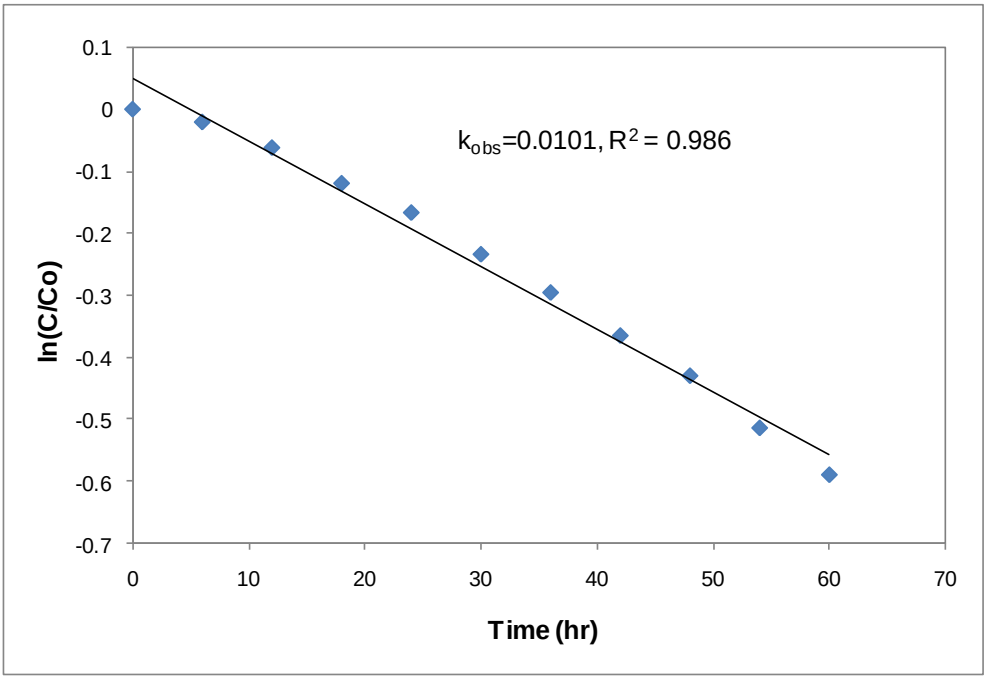

Figure 3: Metolachlor Direct Photolysis

Sunlight induced indirect photolysis significantly enhanced metolachlor degradation in all four wetland waters at either pH 4 or pH 8, as shown in Figures 4 - 7.

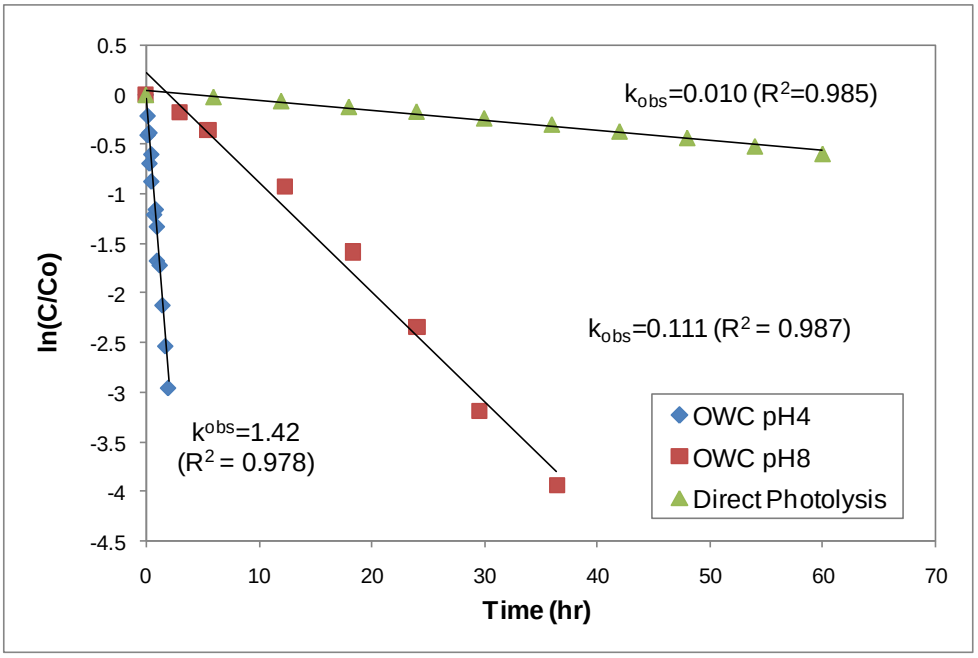

Figure 4: Metolachlor Photodegradation in OWC Water

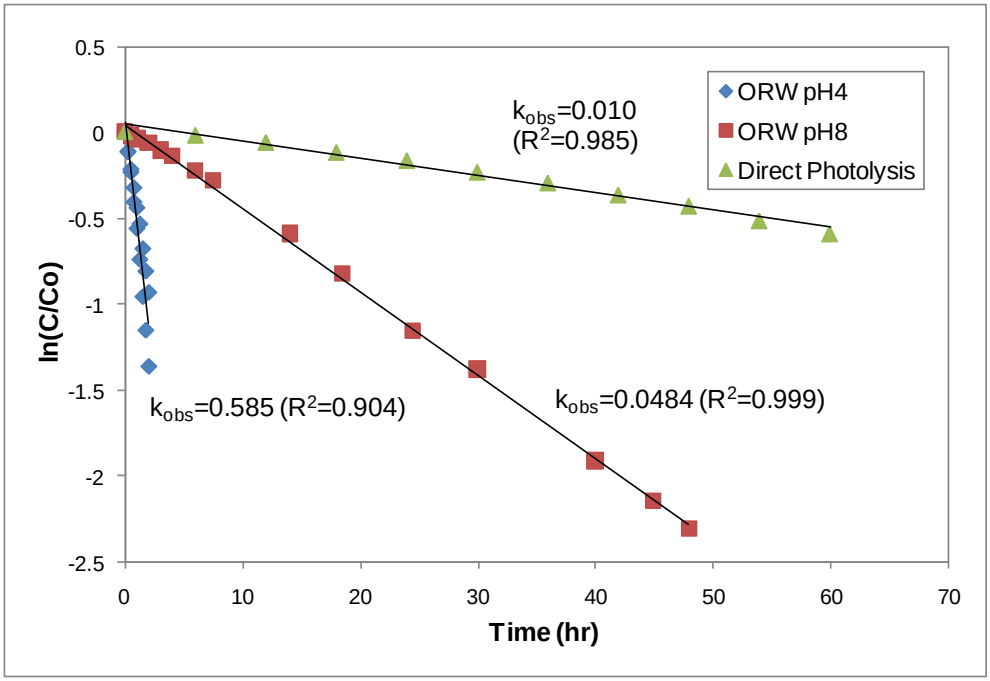

Figure 5: Metolachlor Photodegradation in ORW Water

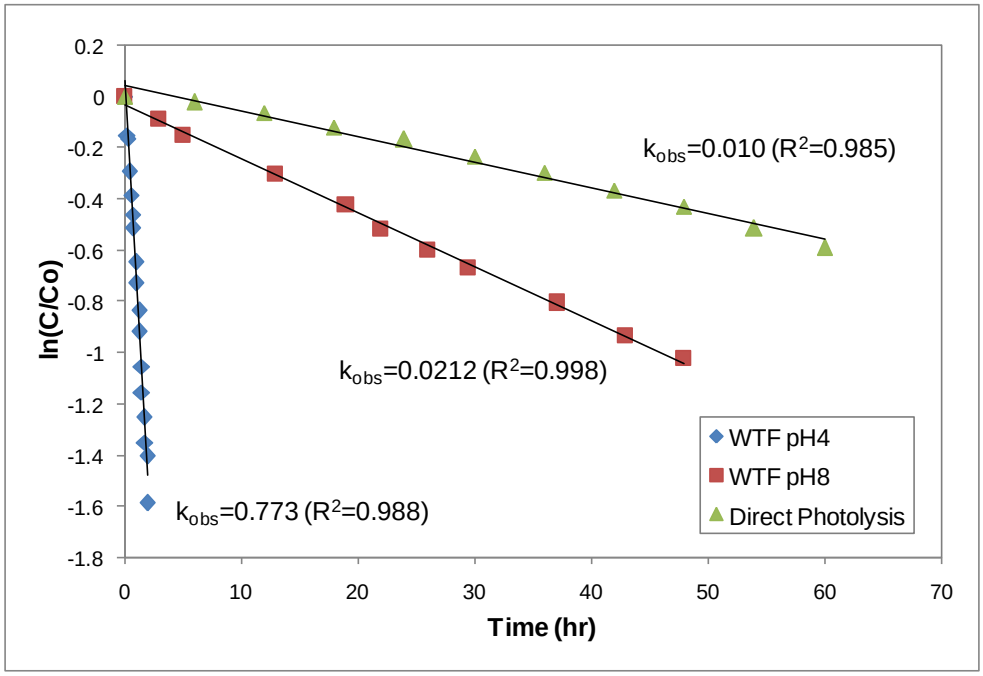

Figure 6: Metolachlor Photodegradation in WTF Water

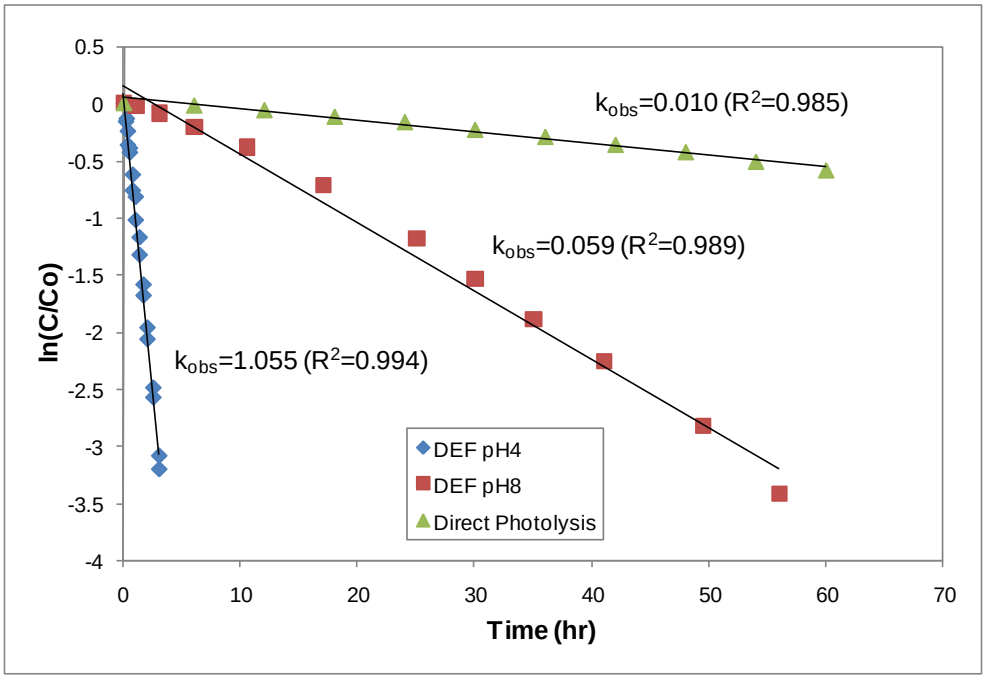

Figure 7: Metolachlor Photodegradation in DEF Water

The pseudo first-order degradation rates of metolachlor in wetland waters at pH 4 were 58 to 141 times greater than the direct photolysis rate constant. At pH 8, the pseudo first-

order degradation rates of metolachlor in wetland waters were 2 to11 times faster than the direct photolysis rate. OWC sample waters acted more effectively than the other sample waters at both pH 4 and pH 8, while the least enhancements were seen in ORW and WTF at pH 4 and pH 8, respectively. Table 2 displays the pseudo first order reaction rate constants and the number of times each rate constant increased compared to the direct photolysis for the wetland waters at pH 4 and pH 8. The equation used to calculate percent increase is shown in Equation 1, where $k_{obs,\ indirect}$ represents the rate constant for the indirect photolysis of metolachlor in a wetland water sample and $k_{obs,\ direct}$ represents the rate constant for the direct photolysis of metolachlor in deionized water.

$$Enhancement\ Factor = \frac{k_{obs,\ indirect}}{k_{obs,\ direct}} \quad (1)$$

Table 2: Pseudo First Order Rate Constants and the Number of Times Each Rate Increased Compared to Direct Photolysis for Wetland Waters

	Direct	OWC		ORW		WTF		DEF	
	k_{obs} (hr^{-1})	k_{obs} (hr^{-1})	Enhancement Factor	k_{obs} (hr^{-1})	Enhancement Factor	k_{obs} (hr^{-1})	Enhancement Factor	k_{obs} (hr^{-1})	Enhancement Factor
pH 4	N/A	1.42	141	0.585	58	0.773	77	1.05	104
pH 8	0.0101	0.111	11	0.0484	5	0.0212	2	0.0599	6

The difference in reaction degradation rates at pH 4 and pH 8 is related to the reduction of Fe(III) to Fe(II). Under acidic conditions, Fe(III) is reduced faster to Fe(II), which participates in Fenton reactions to generate hydroxyl radical (·OH) (Southworth and Voelker, 2003). UV-Vis absorbance indicates the amount of light screening that occured in the wetland waters. The amount of light screening is inversely proportional to the increase in degradation rate compared to direct photolysis for the wetland waters. The wetland waters that had the greatest amount of light screening experienced the least enhancements by indirect photolysis. OWC had less light absorbance compared to the other wetlands and had the greatest enhancement factors for both pH 4 and pH 8.

Addition of Iron to Wetland Waters

The effect of iron addition on metolachlor degradation in OWC can be found in Figure 8.

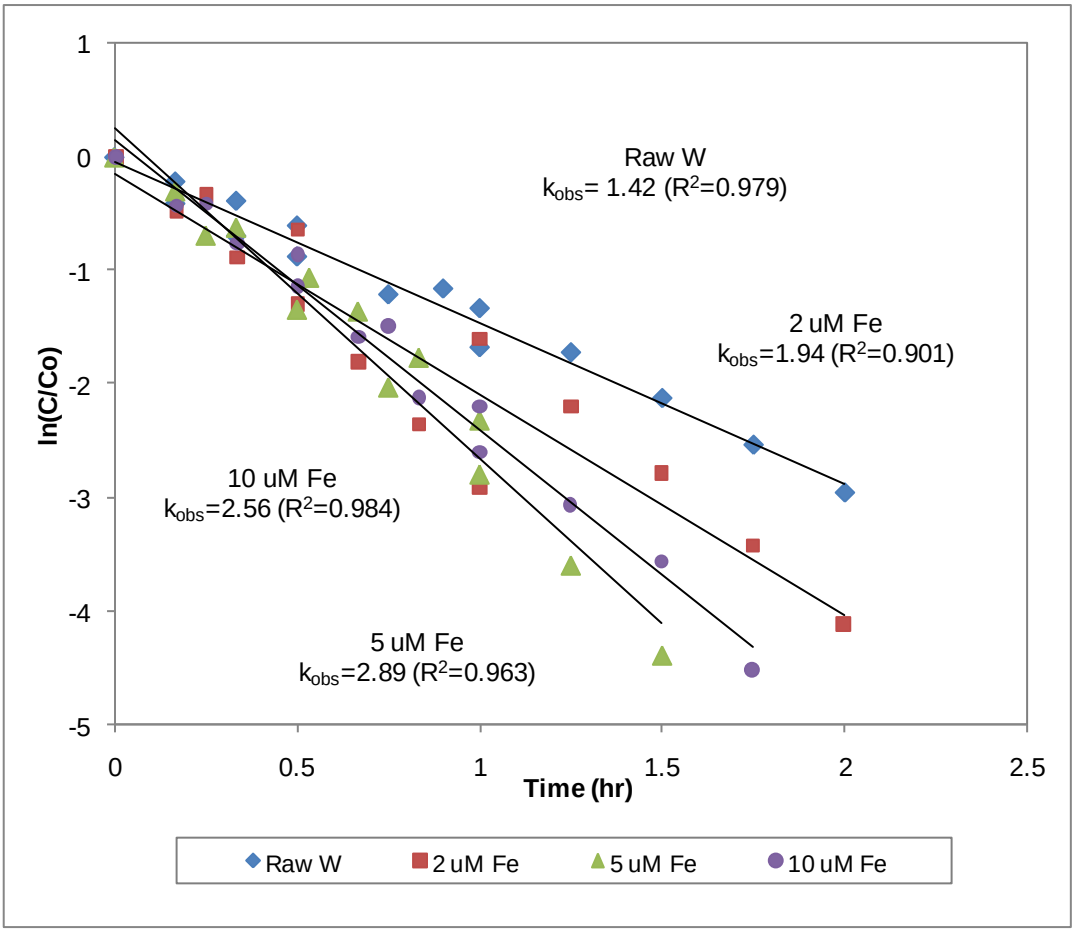

Figure 8: The Effect of Iron Addition on Metolachlor Degradation in OWC Sample Water

Compared to the original 12 µM iron concentration in OWC sample water, the addition of small amounts of iron (2 µM) to OWC sample water enhanced metolachlor degradation rate k_{obs} from 1.4 hr^{-1} to 1.9 hr^{-1} at pH 4. Further additions of iron in OWC did not continue to significantly enhance metolachlor degradation rates. No significant effect was observed at pH 8. The enhancement of metolachlor degradation by addition of iron was contributed to the role of iron in Fenton reactions with reactive species

generated from NOM or iron-NOM complexes by photolysis. The increase in degradation rates was not proportional to the addition of iron suggesting that iron was at saturation in its photosensitizing role. In OWC and DEF, Miller and Chin observed similar results in the degradation of alachlor (2005). As shown in Figure 9, the addition of iron to constructed wetland waters slightly (ORW and DEF) or barely (WTF) enhanced metolachlor degradation at pH 4, but the increase was not as obvious as in OWC water. The constructed wetlands (ORW, WTF, and DEF) have greater concentrations of DOM compared to the natural wetland, OWC. The iron in the constructed wetland waters may be complexed with the DOM and unavailable to generate reactive oxygen species. Further studies are needed to see if the constructed wetland systems need higher concentrations of added iron to further enhance metolachlor degradation by indirect photolysis. Additionally, OWC water experienced less light screening effects compared to the constructed wetland waters.

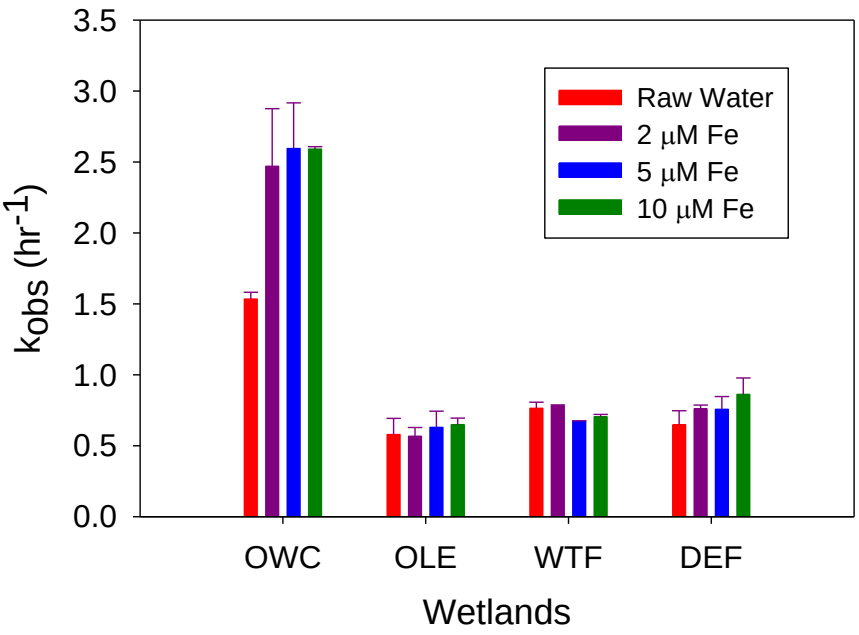

Figure 9: The Effect of Iron Addition on Metolachlor Degradation in Natural Wetland Water (OWC) and Constructed Wetland Waters (ORW, WTF, DEF)

CONCLUSIONS

This study determined the nature and abundance of photosensitizers (DOM, nitrate, and iron) present in one natural wetland and three constructed wetlands, investigated the sunlight induced degradation of metolachlor in the four wetland waters, and examined the addition of iron to wetland waters as a means of promoting the photodegradation of metolachlor. Metolachlor degradation was enhanced 58 to 141 times at pH 4 and 2 to 11 times at pH 8 in wetland waters compared to direct photolysis in deionized water, with Old Woman Creek water acting most effectively. The addition of 2-10 μM of iron promoted metolachlor degradation in Old Woman Creek water by 37-100% at pH 4, while no significant enhancements were observed for other wetland waters. Further studies are necessary to measure the production of reactive oxygen species and monitor iron speciation variation under different conditions to understand the role of iron addition.

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